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Synthesis, reactivity and catalytic activity in transfer hydrogenation of ketones of ruthenium(II) and ruthenium(IV) complexes containing the novel *N*-thiophosphorylated iminophosphorane-phosphine ligands $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et, Ph)†

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Iminophosphorane-phosphines $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et **1a**, Ph **1b**) have been prepared by treatment of bis(diphenylphosphino)methane with an equimolar amount of thiophosphorylated azides $(RO)_2P(=S)N_3$. Dimers $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl\}_2]$ and $[\{Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ react with a two-fold excess of **1a**,**b** yielding the neutral complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et **2a**, Ph **2b**) and $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et **5a**, Ph **5b**), respectively. Treatment of **2a**,**b** and **5a**,**b** with one equivalent of $AgSbF_6$ affords the cationic species $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ (R = Et **3a**, Ph **3b**) and $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ (R = Et **6a**, Ph **6b**), respectively. The structure of the cation of complex **6a** has been confirmed by X-ray crystallography. The preference observed for the $\kappa^2\text{-}P,S$- *vs.* $\kappa^2\text{-}P,N$- coordination of **1a**,**b** seems to be sterically controlled since theoretical calculations on the models $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **A** and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,S\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **B** show that isomer **A** is *ca.* 5.0 kcal mol^{-1} more stable than **B**. Dicationic complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]_2$ (R = Et **4a**, Ph **4b**) and $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]_2$ (R = Et **7a**, Ph **7b**) have been obtained by treating **2a**,**b** and **5a**,**b**, respectively, with two equivalents of $AgSbF_6$. The reactivity of $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]_2$ **4a** towards neutral and anionic ligands has been explored allowing the synthesis of complexes $[Ru(\eta^6\text{-}p\text{-cymene})(L)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]_2$ (L = N≡CMe **8**, PMe_3 **9**, PMe_2Ph **10**, $PMePh_2$ **11**) and $[Ru(\eta^6\text{-}p\text{-cymene})X(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]$ (X = Br **12**, I **13**, N_3 **14**), respectively. The catalytic activity of complexes **2**–**7a**,**b** in transfer hydrogenation of ketones by propan-2-ol has been also studied.

Introduction

Since its discovery in 1919,[1] the imination reaction of tertiary phosphines with organic azides, known as the Staudinger reaction, has been widely used for the preparation of iminophosphoranes $R_3P{=}N{-}R'$.[2] Such compounds usually act as neutral monodentate ligands *via* the lone pair at the nitrogen centre.[3–5] Remarkably, the intrinsic coordinating ability of iminophosphoranes, which are predominantly σ-donors with only minor π-acceptor properties, is weak being easily exchanged by other ligands such as phosphines, phosphites, arsines, carbon monoxide or bipyridine.[6]

The selective monoimination of bis-phosphines with azides has been also successfully applied to the preparation of several iminophosphorane-phosphines $R_2P{-}X{-}P(=NR')R_2$ (X = divalent bridging group).[7] These heteroditopic *P,N*-ligands have led to a host of new coordination and organometallic complexes.[7,8] Moreover, the contrasting (*e.g.* hard/soft) reactivities of their two donor centers confer on these ligands hemilabile properties of interest from a reactivity and catalytic point of view.[9,10] Nevertheless, despite its great potential, their involvement in homogeneous catalysis still remains scarcely explored.[11]

As part of our current work dealing with the chemistry of ruthenium complexes containing $R_2P{-}X{-}P(=NR')R_2$ ligands,[10,11f] we have recently reported the preparation of the heterotrifunctional iminophosphorane-phosphines $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et, Ph).[12] These ligands have shown a versatile coordination ability in ruthenium fragments adopting $\kappa^1\text{-}P$- (**I**), $\kappa^2\text{-}P,N$- (**II**), $\kappa^2\text{-}P,O$- (**III**) and $\kappa^3\text{-}P,N,O$-coordination modes (**IV**) (see Chart 1).

Although theoretical calculations (DFT level) on the model complexes $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ predicted that the $\kappa^2\text{-}P,N$-isomers **II** are more stable than their $\kappa^2\text{-}P,O$-counterparts **III**, a marked preference for the bidentate $\kappa^2\text{-}P,O$-coordination, due probably to steric reasons, was experimentally observed.[12]

Continuing with these studies, in this paper we report on the synthesis, reactivity and catalytic activity in transfer hydrogenation of ketones of Ru(II) and Ru(IV) complexes containing the closely related *N*-thiophosphorylated iminophosphorane-phosphine ligands $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et **1a**, Ph **1b**) in which the coordinating phosphoryl $(RO)_2P{=}O$ substi-

† Electronic supplementary information (ESI) available: analytical and spectroscopic data. See http://www.rsc.org/suppdata/dt/b3/b305520e/

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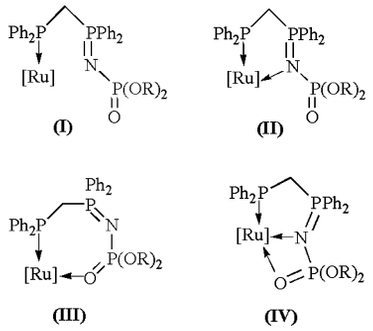


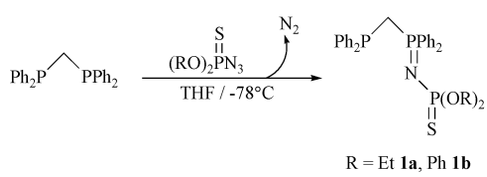
Chart 1 Coordination modes of iminophosphorane-phosphine ligands $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ in ruthenium fragments.

tuents have been replaced by the softer thiophosphoryl $(RO)_2P=S$ units. For comparative purposes, theoretical calculations on the models $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,S\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ are also discussed.

Results

Synthesis of iminophosphorane-phosphine ligands $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et 1a, Ph 1b)

Thiophosphoryl azides $(RO)_2P(=S)N_3$ (R = Et, Ph)[13] react with bis(diphenylphosphino)methane (dppm) (1 : 1 molar ratio), in THF at −78 °C, to afford the novel (*N*-thiophosphoryl-iminophosphoranyl)(phosphino)methane ligands $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et **1a**, Ph **1b**), which have been isolated as air-stable white microcrystalline solids in 94 and 89% yield, respectively (Scheme 1).

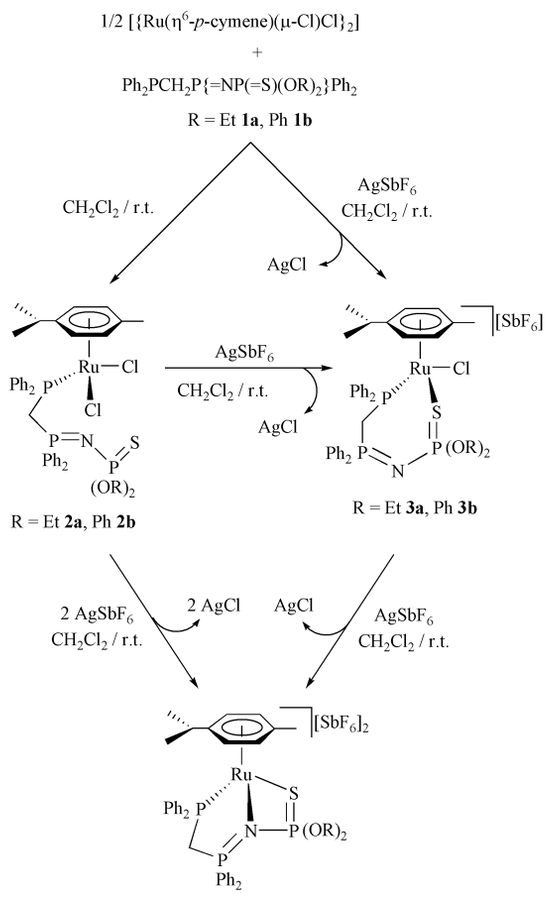


Scheme 1 Synthesis of iminophosphorane-phosphine ligands **1a**,**b**.

Characterization of **1a**,**b** was straightforward following their analytical and spectroscopic data. Thus, the $^{31}P\text{–}\{^1H\}$ NMR spectra show three well separated signals with equal relative intensities (δ_P **1a**: −27.18 (d, $^2J(PP) = 62.7$ Hz, Ph_2P), 15.66 (dd, $^2J(PP) = 62.7$ and 32.1 Hz, $Ph_2P{=}N$) and 60.63 (d, $^2J(PP) = 32.1$ Hz, $(EtO)_2P{=}S$); **1b**: −27.58 (d, $^2J(PP) = 63.4$ Hz, Ph_2P), 17.15 (dd, $^2J(PP) = 63.4$ and 33.6 Hz, $Ph_2P{=}N$) and 52.93 (d, $^2J(PP) = 33.6$ Hz, $(PhO)_2P{=}S$)). The chemical shifts as well as the coupling constants can be compared with those described in the literature for related iminophosphorane compounds $Ph_2P\text{-}CH_2P(=NR)Ph_2$[7] and $R_3P{=}NP(=S)(OR')_2$.[14] In their ^1H NMR spectra the methylenic PCH_2P hydrogens resonate as a doublet (*ca.* 3.6 ppm) due to their coupling with the phosphorus atom of the $Ph_2P{=}N$ unit (*ca.* $^2J(HP) = 14$ Hz). As previously reported for their phosphoryl counterparts $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et, Ph),[12] no coupling with the Ph_2P phosphorus nucleus, usually in the range $^2J(HP) = 1$–3 Hz for related $Ph_2PCH_2P(=NR)Ph_2$ ligands,[7] was observed. The methylenic PCH_2P carbon appears in the $^{13}C\text{–}\{^1H\}$ NMR as a doublet of doublets signal (*ca.* $^1J(CP) = 64$ and 34 Hz; coupling with the P^V and P^{III} nuclei, respectively) at *ca.* 28 ppm.

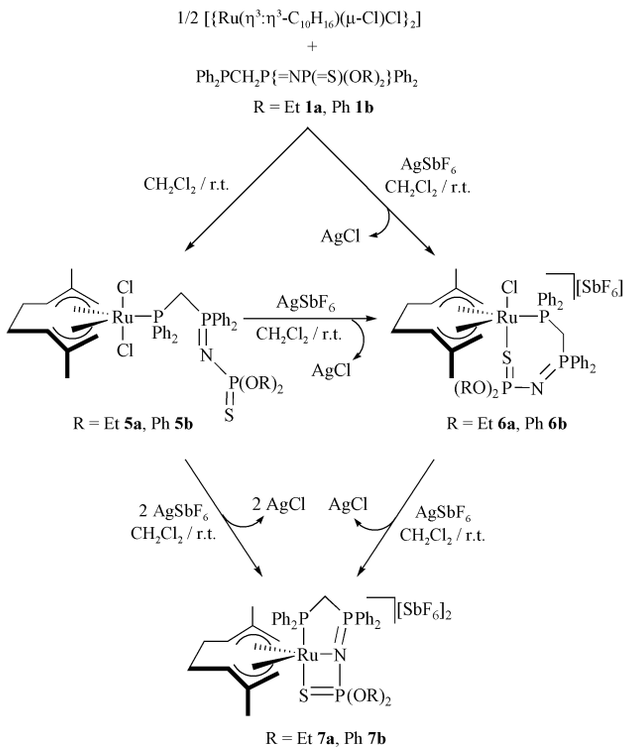
Coordination of thiophosphorylated ligands $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et 1a, Ph 1b) to ruthenium(II) and ruthenium(IV) fragments

(a) Synthesis of κ^1-*P*-complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et 2a, Ph 2b) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et 5a, Ph 5b). Treatment of the dimeric complexes $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl\}_2]$[15] and $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$[16] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) with two equivalents of **1a**,**b**, in dichlorometane at room temperature, selectively affords the monomeric derivatives $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et **2a**, Ph **2b**; Scheme 2) and $[Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et **5a**, Ph **5b**; Scheme 3), respectively, which have been isolated as air-stable orange microcrystalline solids in very good yields (89–98%).



Scheme 2 Coordination of iminophosphorane-phosphine ligands **1a**,**b** on a (η^6-arene)-ruthenium(II) moiety.

An unequivocal proof of the monohapto coordination of **1a**,**b** through the diphenylphosphino group in complexes **2a**,**b** and **5a**,**b** is provided by their $^{31}P\text{–}\{^1H\}$ NMR spectra. Thus, the Ph_2P signal appears in the range δ 20.30–23.94 (d, $^2J(PP) = 37.4$–39.3 Hz), remarkably deshielded in relation to the free ligands **1a**,**b** (*ca.* $\Delta\delta$ 48 ppm). In contrast, a slight shielding is observed in the resonances corresponding to the iminophosphorane $Ph_2P{=}N$ units (δ 11.58–13.53 (dd, $^2J(PP) = 37.4$–39.3 and 23.4–27.9 Hz); $\Delta\delta$ −4 ppm) and the thiophosphoryl $(RO)_2P{=}S$ groups (δ 51.69–59.68 (d, $^2J(PP) = 23.4$–27.9 Hz); $\Delta\delta$ −1 ppm). ^1H and $^{13}C\text{–}\{^1H\}$ NMR spectra are also consistent with the proposed formulations (details are given in the ESI †). In particular, the methylenic PCH_2P protons and carbons appear at δ 3.87–4.43 (**2a**,**b**: one doublet of doublets signal, $^2J(HP) = 9.4$–9.8 Hz; **5a**,**b**: two unresolved multiplets) and 20.30–25.02 (ddd, $^1J(CP) = 71.6$–75.5 (P^V) and 15.1–18.9 (P^{III}) Hz, $^3J(CP) = 4.7$–6.4 Hz) ppm, respectively. Noteworthy, the protons of the 2,7-dimethylocta-2,6-diene-1,8-diyl chain in the ruthenium(IV) complexes **5a**,**b** give rise to only six resonances and their carbon atoms to five in the NMR spectra, suggesting that the two halves of the bis(allyl) ligand are in equivalent environments, as expected for the formation of a simple equatorial adduct with C_2-symmetry.[16]



Scheme 3 Coordination of iminophosphorane-phosphine ligands **1a**,**b** on a bis(allyl)-ruthenium(IV) moiety.

(b) Synthesis of κ²-*P,S*-complexes [Ru(η⁶-*p*-cymene)Cl(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OR)_2$}Ph_2)][SbF_6] (R = Et 3a, Ph 3b) and [Ru(η³:η³-$C_{10}H_{16}$)Cl(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)-$(OR)_2$}Ph_2)][SbF_6] (R = Et 6a, Ph 6b). Treatment of dichloromethane solutions of neutral complexes **2a**,**b** and **5a**,**b** with 1 equiv. of silver hexafluoroantimonate results in the formation of the cationic derivatives [Ru(η⁶-*p*-cymene)Cl(κ²-*P,S*-Ph_2-PCH_2P{=NP(=S)$(OR)_2$}Ph_2)][SbF_6] (R = Et **3a**, Ph **3b**; Scheme 2) and [Ru(η³:η³-$C_{10}H_{16}$)Cl(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OR)_2$}-Ph_2)][SbF_6] (R = Et **6a**, Ph **6b**; Scheme 3), respectively, *via* selective *S*-coordination of the free *N*-thiophosphoryl-iminophosphoranyl fragment (80–96% yield). As expected, these complexes can be also prepared in similar yields from dimers [{Ru(η⁶-*p*-cymene)(μ-Cl)Cl}$_2$] and [{Ru(η³:η³-$C_{10}H_{16}$)(μ-Cl)-Cl}$_2$] by reaction with 2 equiv. of **1a**,**b** and $AgSbF_6$ in dichloromethane at room temperature (see Schemes 2 and 3).

Compounds **3a**,**b** and **6a**,**b** have been isolated as air-stable orange microcrystalline solids. They have been characterized by elemental analyses, conductance measurements, and IR and NMR spectroscopy (see the ESI† for details). Moreover, the formation of seven-membered chelate rings was unambiguously confirmed by a X-ray diffraction study on the cation of complex **6a**.[17] A drawing of the molecular structure is depicted in Fig. 1; selected bond distances and angles are listed in the caption. The geometry about the ruthenium(IV) centre can be described as a distorted trigonal bipyramid (*TBPY*) by considering the allyl groups as monodentate ligands bound to ruthenium through their centres of mass (C* and C**; see caption for Fig. 1). The iminophosphorane-phosphine ligand **1a** is coordinated edge-on to the metal through the P atom of the diphenylphosphino unit, which resides in an equatorial position along with the allyl groups, and the thiophosphoryl S atom, which is *trans* to the chloride ligand in an axial position. The Ru–S bond length (2.437(3) Å) is typical for *S*-coordinated thiophosphorus ligands.[18] We note that an analogous arrangement was shown by its phosphoryl counterpart [Ru(η³:η³-$C_{10}H_{16}$)Cl(κ²-*P,O*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)]$^+$, in which the oxygen atom also occupies an axial position *trans* to the chloride ligand.[12] Both allyl groups of the octadienediyl fragment are η³-bound to the ruthenium atom with Ru–C and C–C

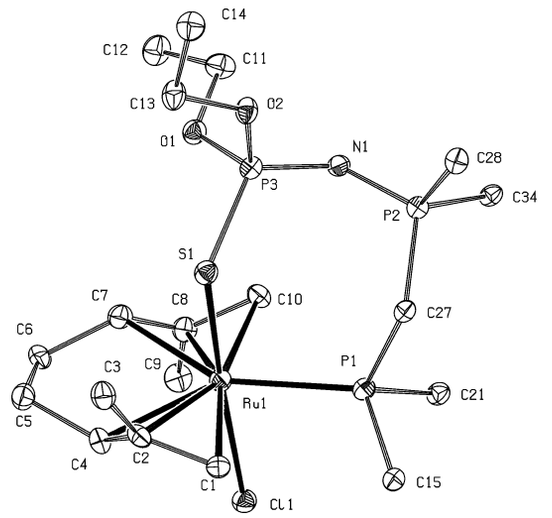


Fig. 1 ORTEP-type view of the structure of the cation [Ru(η³:η³-$C_{10}H_{16}$)Cl(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)]$^+$ of **6a** showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings of the Ph_2P groups are shown. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths (Å) and angles (°): Ru–C(1) = 2.242(9); Ru–C(2) = 2.332(9); Ru–C(4) = 2.297(9); Ru–C* = 2.038(11); C(1)–C(2) = 1.422(13); C(2)–C(4) = 1.409(13); Ru–C(7) = 2.321(9); Ru–C(8) = 2.289(9); Ru–C(10) = 2.254(9); Ru–C** = 2.038(9); C(7)–C(8) = 1.390(14); C(8)–C(10) = 1.426(13); Ru–P(1) = 2.444(2); Ru–S(1) = 2.437(3); Ru–Cl(1) = 2.441(4); P(1)–C(27) = 1.857(9); C(27)–P(2) = 1.816(9); P(2)–N(1) = 1.591(7); N(1)–P(3) = 1.573(8); P(3)–O(1) = 1.576(7); P(3)–O(2) = 1.579(7); P(3)–S(1) = 1.995(4); C*–Ru–C** = 130.0(4); C*–Ru–S(1) = 87.0(3); C**–Ru–S(1) = 95.5(3); C*–Ru–Cl(1) = 87.8(3); C**–Ru–Cl(1) = 94.0(3); C*–Ru–P(1) = 114.8(4); C**–Ru–P(1) = 115.0(3); S(1)–Ru–P(1) = 92.02(8); S(1)–Ru–Cl(1) = 170.39(8); P(1)–Ru–Cl(1) = 82.84(8); Ru–P(1)–C(27) = 114.7(3); Ru–P(1)–C(15) = 113.4(3); Ru–P(1)–C(21) = 123.5(3); P(1)–C(27)–P(2) = 123.9(5); C(27)–P(2)–N(1) = 114.4(4); C(27)–P(2)–C(28) = 104.1(4); C(27)–P(2)–C(34) = 112.3(4); P(2)–N(1)–P(3) = 130.3(5); N(1)–P(3)–O(1) = 107.9(4); N(1)–P(3)–O(2) = 108.1(4); N(1)–P(3)–S(1) = 118.3(3); O(1)–P(3)–S(1) = 107.7(3); O(1)–P(3)–O(2) = 107.1(4); O(2)–P(3)–S(1) = 107.2(3); P(3)–S(1)–Ru = 115.5(2). C* and C** = centroids of the allyl units (C(1), C(2), C(4) and C(7), C(8), C(10), respectively).

distances in the ranges 2.242(9)–2.332(9) and 1.390(14)–1.426(13) Å, respectively (see caption for Fig. 1). These values, together with the internal allylic C–C–C angles (117.1(9)° and 116.5(9)°), compare well with those observed in other structures containing the "Ru(η³:η³-$C_{10}H_{16}$)" unit.[16] Concerning the iminophosphorane-phosphine ligand backbone, the most remarkable feature is that the lengths of the formal single and double PN bonds were found to be very similar (1.573(8) Å and 1.591(7) Å, respectively). This apparent discrepancy, which seems to be a usual trend in iminophosphorane compounds $R_3P{=}N{-}P(=X)(OR')_2$ (X = O, S),[7f,12,14,19] is attributed to the strong withdrawing effect of the thiophosphoryl group which enhances the π delocalization of the lone pair of electrons on nitrogen within the P–N–P unit. The P=S bond distance (1.995(4) Å) is comparable to those found by Majoral and coworkers in dendritic molecules containing P=N–P=S⟶AuCl moieties.[20]

NMR spectroscopic data of complexes **3a**,**b** and **6a**,**b** are consistent with the κ²-*P,S*-coordination of the ligands and, in particular, the chelate ring formation is clearly reflected in the $^{31}P{-}\{^1H\}$ NMR spectra. Thus, as a common trend, when the spectra of **3a**,**b** and **6a**,**b** are compared to those of their neutral precursors **2a**,**b** and **5a**,**b** slight shifts of the $(RO)_2P{=}S$ and $Ph_2P{=}N$ resonances are observed, *i.e.* to highfield (*ca.* $\Delta\delta$ −5 ppm) for the former (dd or d; δ_P = 46.38–54.92; ^2J(PP) = 24.9–28.3 Hz, ^3J(PP) = 0–10.7 Hz) and to downfield ($\Delta\delta$ 0.5 to 4 ppm) for the latter (dd or d; δ_P = 13.12–15.52; ^2J(PP) = 24.9–28.3 and 0–3.8 Hz). The diphenylphosphino group resonances are also affected by the ring closure but, surprisingly, while for

ruthenium(II) complexes **3a**,**b** they are *ca.* 3 ppm downfield shifted (dd signal; *ca.* δ_P = 26; ^3J(PP) = 4.9–10.7 Hz, ^2J(PP) = 3.8 Hz), in their ruthenium(IV) counterparts **6a**,**b** they are high-field shifted ($\Delta\delta$ −6 to −12 ppm; s signal; δ_P = 8.33–14.42). Nevertheless, these chemical shifts, along with those of the Ph_2P=N group, are in accord with the κ²-*P,S*-coordination of **1a**,**b** since we have recently reported that in κ²-*P,N*-complexes [Ru(η⁶-*p*-cymene)Cl{κ²-*P,N*-Ph_2PCH_2P(=NR)Ph_2}]$^+$ and [Ru(η³:η³-$C_{10}H_{16}$)Cl{κ²-*P,N*-Ph_2PCH_2P(=NR)Ph_2}]$^+$ (R = H, aryl group) the Ph_2P=N and Ph_2P phosphorus atoms resonate at *ca.* 54 and 47 ppm, respectively.[10,11f,21] In agreement with the stereogenicity of the metal, the PCH_2P protons are, in all the cases, chemically inequivalent appearing as two unresolved multiplets at δ_H 3.15–5.63. In contrast to **2a**,**b** and **5a**,**b**, the PCH_2P carbon resonates in the ^{13}C–{^1H} NMR spectra as a doublet of doublets, due to exclusive coupling with the Ph_2P=N (^1J(CP) = 56.2–64.0 Hz) and Ph_2P (^1J(CP) = 7.6–16.9 Hz) units, in the range 26.75–29.31 ppm. ^1H and ^{13}C–{^1H} NMR spectra of **6a**,**b** indicate that the two halves of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand are now in inequivalent environments (*i.e.* ten different signals are observed by ^{13}C–{^1H} NMR spectroscopy), as expected for the loss of the C_2 symmetry.

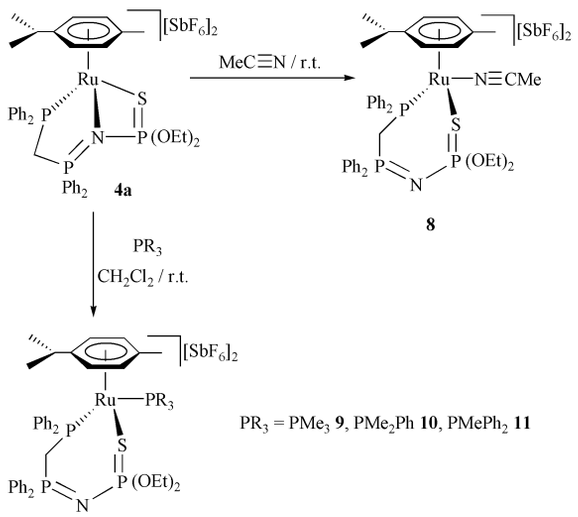
(c) Synthesis of κ³-*P,N,S*-complexes [Ru(η⁶-*p*-cymene)(κ³-*P,N,S*-Ph_2PCH_2P{=NP(=S)$(OR)_2$}Ph_2)][SbF_6]$_2$ (R = Et 4a, Ph 4b) and [Ru(η³:η³-$C_{10}H_{16}$)(κ³-*P,N,S*-Ph_2PCH_2P{=NP(=S)$(OR)_2$}Ph_2)][SbF_6]$_2$ (R = Et 7a, Ph 7b). The reaction of neutral complexes **2a**,**b** and **5a**,**b** with two equivalents of $AgSbF_6$, in dichloromethane at room temperature, generates the dicationic derivatives [Ru(η⁶-*p*-cymene)(κ³-*P,N,S*-Ph_2PCH_2P{=NP(=S)$(OR)_2$}Ph_2)][SbF_6]$_2$ (R = Et **4a**, Ph **4b**; Scheme 2) and [Ru(η³:η³-$C_{10}H_{16}$)(κ³-*P,N,S*-Ph_2PCH_2P{=NP(=S)$(OR)_2$}Ph_2)][SbF_6]$_2$ (R = Et **7a**, Ph **7b**; Scheme 3), respectively, which have been isolated as air-stable yellow (**7a**,**b**) or orange (**4a**,**b**) solids in 78–96% yield. Alternatively, these compounds can be also obtained by treatment of cationic complexes **3a**,**b** and **6a**,**b** with 1 equiv. of $AgSbF_6$ (see Schemes 2 and 3).

Conductance measurements in acetone (Λ_M = 184–197 Ω^{-1} cm^2 mol^{-1}) confirm that compounds **4a**,**b** and **7a**,**b** are 2 : 1 electrolytes (*vs.* 118–135 Ω^{-1} cm^2 mol^{-1} found for **3a**,**b** and **6a**,**b**). ^{31}P–{^1H} NMR spectra clearly indicate the coordination of the iminophosphorane function to ruthenium showing characteristic downfield resonances for the Ph_2P=N (δ_P 44.47–55.69; dd, ^2J(PP) = 21.9–32.6 (P^V) and 9.8–28.3 (P^{III}) Hz) and Ph_2P (δ_P 30.90–43.38; dd, ^2J(PP) = 9.8–28.3 Hz and ^3J(PP) = 4.5–9.8 Hz) phosphorus nuclei,[21] the $(RO)_2P$=S resonances appearing at the expected chemical shifts (δ_P 46.46–56.95; dd, ^2J(PP) = 21.9–32.6 Hz and ^3J(PP) = 4.5–9.8 Hz). ^1H and ^{13}C–{^1H} NMR spectra are also consistent with the proposed formulations (see the ESI †). In particular, the PCH_2P protons and carbon resonate at 3.98–5.17 ppm (two unresolved multiplets) and 25.10–34.26 ppm (dd (**4a**,**b**) or ddd (**7a**,**b**); ^1J(CP) = 67.3–93.7 (P^V) and 17.8–19.3 (P^{III}) Hz, ^3J(CP) = 0–8.3 Hz), respectively.

Reactivity of complex [Ru(η⁶-*p*-cymene)(κ³-*P,N,S*–Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6]$_2$ 4a towards neutral and anionic ligands

In order to compare the hemilabile properties of the thiophosphoryl ligands **1a**,**b** in their κ³-*P,N,S*-coordination mode with those of the κ³-*P,N,O*-coordinated phosphoryl counterparts Ph_2PCH_2P{=NP(=O)$(OR)_2$}Ph_2 [12] the reactivity of the dicationic complex [Ru(η⁶-*p*-cymene)(κ³-*P,N,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6]$_2$ **4a** has been studied.

(a) Synthesis of κ²-*P,S*-complexes [Ru(η⁶-*p*-cymene)(L)(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6]$_2$ (L = N≡CMe 8, PMe_3 9, PMe_2Ph 10, $PMePh_2$ 11). We have found that Ru–N bond cleavage easily takes place when complex **4a** is dissolved in acetonitrile at room temperature, affording the stable solvate [Ru(η⁶-*p*-cymene)(N≡CMe)(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6]$_2$ **8** which has been isolated in 83% yield (Scheme 4). Similarly, treatment of **4a** with an excess of monodentate phosphines (*ca.* 10 equiv.), in dichloromethane at room temperature, generates the dicationic compounds [Ru(η⁶-*p*-cymene)(PR_3)(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6]$_2$ (PR_3 = PMe_3 **9**, PMe_2Ph **10**, $PMePh_2$ **11**) *via* selective Ru–P–N chelate ring opening (80–96% yield; Scheme 4).



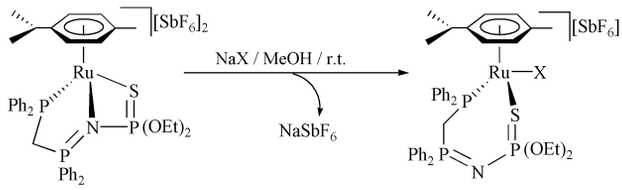
Scheme 4 Reactivity of complex **4a** towards neutral ligands.

Conductance measurements, as well as analytical and spectroscopic data, for **8**–**11** are in agreement with the proposed structures (see the ESI †). In particular, the ^{31}P–{^1H} NMR spectra clearly reveal the presence of uncoordinated Ph_2P=N units (δ_P 13.48–20.64; dd, ^2J(PP) = 27.6–30.7 (P^V) and 5.0–12.7 (P^{III}) Hz).[21] The spectra of complexes **9**–**11** also show the expected resonances of the monodentate PR_3 ligands which appear as a doublet of doublets signal (0.78–4.39 ppm) due to coupling with the coordinated Ph_2P (^2J(PP) = 41.5–49.7 Hz) and $(EtO)_2P$=S (^3J(PP) = 33.4–37.1 Hz) units. It is interesting to note that the NMR spectra of complex **8** indicate that no reversible process involving dissociation–recoordination of the acetonitrile ligand occurs.

Remarkably, all attempts to promote a similar ring opening reaction with acetone have failed recovering the starting complex **4a** unchanged even under prolonged reflux in this solvent. This result contrasts with the behaviour previously observed for the phosphoryl compound [Ru(η⁶-*p*-cymene)(κ³-*P,N,O*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)][SbF_6]$_2$ which reversibly generates the solvato complex [Ru(η⁶-*p*-cymene)(κ¹-*O*-Me_2CO)(κ²-*P,O*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)][SbF_6]$_2$ in acetone at room temperature.[12]

(b) Synthesis of κ²-*P,S*-complexes [Ru(η⁶-*p*-cymene)X(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6] (X = Br 12, I 13, N_3 14). Complex **4a** also reacts, *via* selective Ru–N bond cleavage, with an excess (*ca.* 10 equiv.) of sodium salts NaX, in methanol at room temperature, to afford the cationic derivatives [Ru(η⁶-*p*-cymene)X(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)$(OEt)_2$}Ph_2)][SbF_6] (X = Br **12**, I **13**, N_3 **14**) which have been isolated as air-stable orange microcrystalline solids in excellent yield (89–96%; Scheme 5). We note that neutral complexes [Ru(η⁶-*p*-cymene)X_2(κ¹-*P*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)] (X = Cl, Br, I, N_3) were exclusively obtained when similar reactions were conducted starting with [Ru(η⁶-*p*-cymene)(κ³-*P,N,O*-Ph_2PCH_2P{=NP(=O)$(OEt)_2$}Ph_2)][SbF_6]$_2$.[12]

The novel complexes **12**–**14** have been characterized by elemental analysis, conductance measurements, and IR and NMR (^1H, ^{31}P–{^1H} and ^{13}C–{^1H}) spectroscopy (see the ESI †). Since their spectroscopic data are comparable to those observed for **3a**, they will not be discussed further.



4a

Scheme 5 Reactivity of complex **4a** towards anionic ligands.

Discussion

Novel trifunctional *N*-thiophosphoryl iminophosphorane-phosphine ligands $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et **1a**, Ph **1b**) have been readily obtained by selective monooxidation of dppm with thiophosphorylated azides $(RO)_2P(=S)N_3$ (R = Et, Ph), *via* a conventional Staudinger reaction (see Scheme 1). The selectivity observed in these imination processes probably stems from the proximity of the two Ph_2P groups which hinders the oxidation at the second phosphorus atom for steric reasons.[22] Nevertheless, in order to avoid the formation of the corresponding bis(iminophosphorane) derivatives $CH_2[P\{=NP(=S)(OR)_2\}Ph_2]_2$,[23] a careful control of the temperature (−78 °C) is required as well as the use of a rigorous stoichiometric amount of the azides.

Compounds **1a**,**b** are versatile ligands for ruthenium(II) and ruthenium(IV) fragments derived from the readily available chloro-bridged dimeric species $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl\}_2]$ and $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$, respectively. As shown in Schemes 2 and 3 they are able to adopt three different types of coordination mode: (*i*) monodentate κ^1-*P* in neutral complexes **2a**,**b** and **5a**,**b**, (*ii*) bidentate κ^2-*P,S*-chelate in cationic complexes **3a**,**b** and **6a**,**b**, and (*iii*) tridentate κ^3-*P,N,S*-bis-chelate in dicationic complexes **4a**,**b** and **7a**,**b**. These coordination features reproduce those shown by the phosphoryl ligands $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (R = Et, Ph; see Chart 1),[12] with the exception of the corresponding κ^2-*P,N*-mode (see Fig. 2).

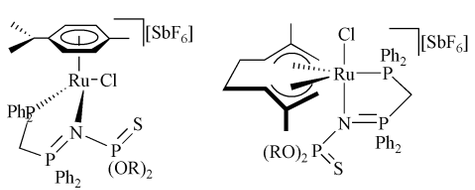


Fig. 2 Potential κ^2-*P,N*-coordination of **1a**,**b**.

In order to account for the preferred formation of the seven- *vs.* five-membered chelate rings (κ^2-*P,S*- *vs.* κ^2-*P,N*-coordination), also observed with their phosphoryl counterparts (κ^2-*P,O*- *vs.* κ^2-*P,N*-coordination),[12] the relative stability of the models $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **A** and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,S\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **B** has been theoretically studied following the methodology used for our previous calculations with the phosphoryl derivatives.[12]

The optimized structures for **A** and **B** with the B3LYP/DZV(d) wave function are shown in Fig. 3, and their relevant geometrical parameters, which compare well with those of the previously optimized models $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$ and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,O\text{-}H_2PCH_2P\{=NP(=O)(OH)_2\}H_2)]^+$,[12] are given in the caption. Both structures were characterized as minima on the potential energy surface, and their absolute and relative energies are listed in Table 1.

Both structures are almost isoenergetic at the B3LYP/DZV(d)//B3LYP/DZV(d) level (see Table 1). Moreover, inclusion of correlation results in a difference of only 5.0 kcal mol^{-1} in favour of the κ^2-*P,N*-isomer **A** (MP2/DZV(d)//B3LYP/DZV(d) level). Remarkably, the values of the interligand angles

Table 1 Absolute (hartrees) and relative (kcal mol^{-1}, parentheses) energies for $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **A** and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,S\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **B** models[a]

Model	B3LYP/DZV(d)	MP2/DZV(d)
A	−618.563254 (0.0)	−615.730363 (0.0)
B	−618.562109 (0.7)	−615.722347 (5.0)

[a] B3LYP/DZV(d)-optimized geometries.

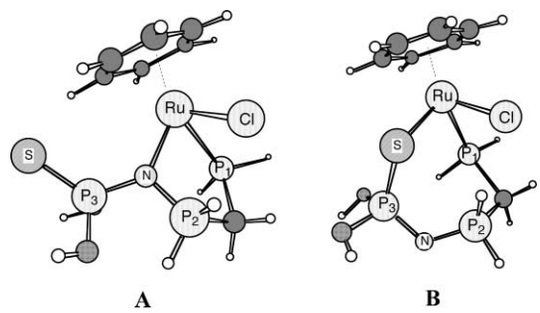
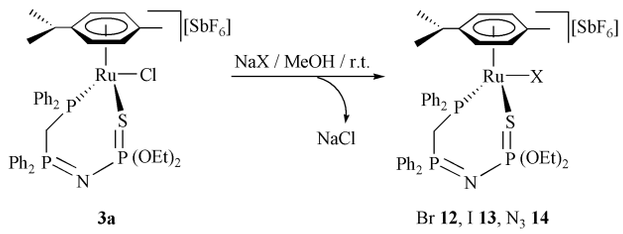


Fig. 3 Computer plot of the B3LYP/DZV(d) optimized structures for the model complexes $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,N\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **A** and $[Ru(\eta^6\text{-}C_6H_6)Cl(\kappa^2\text{-}P,S\text{-}H_2PCH_2P\{=NP(=S)(OH)_2\}H_2)]^+$ **B**. Selected bond lengths (Å) and angles (°) for model **A**: Ru–P_1 = 2.446; P_1–C = 1.907; C–P_2 = 1.878; P_2–N = 1.714; N–Ru = 2.198; Ru–Cl = 2.497; average Ru–C_{arene} = 2.276; Ru–P_1–C = 107.3; P_1–C–P_2 = 107.0; C–P_2–N = 108.7; P_2–N–Ru = 114.3; P_1–Ru–N = 80.6; P_1–Ru–Cl = 80.5; N–Ru–Cl = 86.3. For model **B**: Ru–P_1 = 2.439; P_1–C = 1.899; C–P_2 = 1.871; P_2–N = 1.682; N–P_3 = 1.655; P_3–S = 2.182; S–Ru = 2.533; Ru–Cl = 2.485; average Ru–C_{arene} = 2.278; Ru–P_1–C = 119.0; P_1–C–P_2 = 111.7; C–P_2–N = 113.9; P_2–N–P_3 = 120.8; N–P_3–S = 116.2; P_3–S–Ru = 110.2; P_1–Ru–S = 96.3; P_1–Ru–Cl = 84.3; S–Ru–Cl = 87.5.

P_1–Ru–N (80.6°), P_1–Ru–Cl (80.5°), and N–Ru–Cl (86.3°) in model **A** and P_1–Ru–S (96.3°), P_1–Ru–Cl (84.3°), and S–Ru–Cl (87.5°) in model **B**, which are typical for pseudo-octahedral three-legged piano-stool geometries, indicate similar strain energies for both complexes.[24] Thus, in the absence of marked differences in strain energies between **A** and **B**, the results obtained can be interpreted in terms of a very similar bond energy of the Ru–N and Ru–S bonds. The preferred κ^2-*P,S*- *vs.* κ^2-*P,N*-coordination of **1a**,**b** experimentally observed should be therefore attributed to the higher steric hindrances between the thiophosphoryl group substituents and the η^6-*p*-cymene or $\eta^3{:}\eta^3$-octadienediyl ligands in the five-membered chelates. As we have reported previously,[12] this effect also governs the preference observed for the κ^2-*P,O*- *vs.* κ^2-*P,N*-coordination of the related *N*-phosphoryl iminophosphorane-phosphine ligands in their ruthenium complexes.

However, the relatively small energetic difference found between the five- (**A**) and seven-membered (**B**) chelate complexes contrasts with that obtained in our calculations using the phosphorylated ligand $PH_2CH_2P\{=NP(=O)(OH)_2\}H_2$ (5.0 *vs.* 11.5 kcal mol^{-1}).[12] This fact seems to indicate a higher strength of the Ru—S bond *vs.* the Ru–O one in compounds $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)][SbF_6]$ (X = O, S), in accord with the well-known stability of the Ru–S bonds due to the soft character of the metal atom.

This theoretical prediction is also in accord with the experimental reactivity of these complexes towards anionic ligands. Thus, we have found that treatment of complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]$ **3a** with an excess of sodium salts NaX, in methanol at room temperature, yields the cationic derivatives $[Ru(\eta^6\text{-}p\text{-cymene})X(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]$ (X = Br **12**, I **13**, N_3 **14**) as the result of chloride metathesis (Scheme 6). In contrast, we have previously reported that the analogous complexes $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)][SbF_6]$ (R = Et, Ph), under similar reaction conditions, do not generate $[Ru(\eta^6\text{-}p\text{-cymene})X(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{=NP(=O)$-



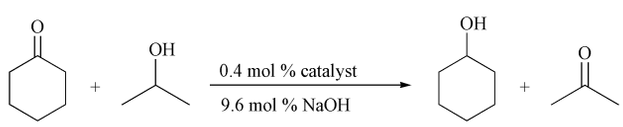
3a Br **12**, I **13**, N_3 **14**

Scheme 6 Reactivity of complex **3a** towards anionic ligands.

$(OR)_2\}Ph_2)][SbF_6]$, giving instead the neutral derivatives $[Ru(\eta^6\text{-}p\text{-cymene})X_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)]$ (X = Br, I, N_3) through a chelate ring opening reaction.[12] The reluctance of **3a** to undergo a cleavage of the Ru–S bond is also assessed in the presence of neutral monodentate phosphines. Thus, after prolonged treatment in dichloromethane at room temperature, the complex **3a** is recovered unchanged.[25] All these experimental data along with: (*i*) the lack of reversibility in the formation of complex **8**, (*ii*) the stability of **4a** in acetone and (*iii*) the selective formation of cationic complexes **12**–**14** from **4a** (Scheme 5), allows one to establish that no hemilabile properties can be associated with these thiophosphorylated derivatives.

Catalytic transfer hydrogenation of ketones

Following our interest in ruthenium-catalyzed hydrogen transfer reactions between alcohols and ketones,[11f,12,26] the catalytic activity in transfer hydrogenation of cyclohexanone by propan-2-ol of ruthenium(II) and ruthenium(IV) complexes **2**–**4a**,**b** and **5**–**7a**,**b**, respectively, has been explored (Scheme 7). Thus, in a typical experiment, the ruthenium catalyst precursor (0.4 mol%) and NaOH (9.6 mol%) were added to a 0.2 M solution of cyclohexanone in ^{i}PrOH at 82 °C, the reaction being monitored by gas chromatography. Selected results are shown in Table 2.



Scheme 7 Catalytic transfer hydrogenation of cyclohexanone by propan-2-ol.

All the complexes tested, as their phosphoryl partners,[12] have proven to be active catalysts for the reduction of cyclohexanone to cyclohexanol. We note that despite the large number of transfer hydrogenation catalysts known,[27] only a few of them contains sulfur ligands and, to the best of our knowledge, no transition-metal catalysts containing tridentate *P,N,S*-ligands have been reported to date.[28]

Results of the catalytic activity collected in Table 2 allows a comparison with those previously reported for the corresponding phosphoryl-ruthenium complexes.[12] In this regard, the following similar trends have been observed in both studies: (*i*) due to steric effects, the catalytic performances shown by the catalysts containing the ligand **1a** (R = Et) are much better than those containing **1b** (R = Ph) both in the Ru(II) and Ru(IV) series (see odd *vs.* even entries), (*ii*) the catalytic activities of the ruthenium(IV) complexes are in all cases higher than those of their corresponding ruthenium(II) counterparts (see entries 1–6 *vs.* 7–12), and (*iii*) whilst the neutral κ^1-*P*-complexes are the most active in the Ru(II) series (entries 1 *vs.* 3 and 5, and 2 *vs.* 4 and 6), the cationic κ^2-*P,S*-derivatives show the best performances in the Ru(IV) series (entries 9 *vs.* 7 and 11, and 10 *vs.* 8 and 12). This seems to point out that there is no direct relationship between the catalytic activity and the coordination mode of the ligands.

It is interesting to note that, in contrast to the similar catalytic efficiencies found for both phosphoryl- and thiophosphoryl-ruthenium(II) complexes (TOF_{50}: 14–70 *vs.* 10–50 h^{-1}; see ref. 12 and Table 2), the ruthenium(IV) derivatives **5**–**7a**,**b** are comparatively more active than their phosphoryl counterparts (TOF_{50}: 150–1600 *vs.* 12–426 h^{-1}; see ref. 12 and Table 2). This is particularly remarkable in the case of the most active ruthenium(IV) complexes $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{=NP(=X)(OEt)_2\}Ph_2)][SbF_6]$ (TOF_{50}: 426 h^{-1} (X =O) *vs.* 1600 h^{-1} (X =S)). Providing that, as was established above, the thiophosphoryl complexes do not show hemilabile properties (in contrast to the phosphoryl ones)[12] it can be concluded that this property does not play a crucial role in the formation of the active species. Although no detailed mechanistic studies have been performed, we have found that the $^{31}P\{^1H\}$-NMR spectrum of the catalytic reaction mixture derived from $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]$ **6a** shows the clean formation of a novel species with resonances at δ_P 14.70 (d, ^2J(PP) = 29.5 Hz, Ph_2P=N), 20.55 (s, Ph_2P) and 61.51 (d, ^2J(PP) = 29.5 Hz, $(EtO)_2P$=S). These chemical shifts and coupling constants seem to indicate the κ^2-*P,S*-coordination of the ligand. Unfortunately, all attempts to isolate this complex failed since after solvent removal a complicated mixture of products is formed. Significantly, no signals attributable to coordinated octadienediyl units were observed in the ^{1}H NMR spectra of this mixture, suggesting that the active species in the catalytic cycle are formed by the release of the bis(allyl) ligand.

In order to check the scope of the catalytic activity of the most active complex **6a**, the hydride transfer hydrogenation of other dialkyl as well as aryl-alkyl ketones has been explored. Results are summarized in Table 3.

Thus, complex **6a** has been shown to be efficient in the reduction of dialkyl ketones (entries 1–4 in Table 3) although its catalytic activity is significantly reduced when bulky substituents are present in the ketone (*i.e.* Me(Et)CO *vs.* Me(^{i}Pr)CO; entry 3 *vs.* 4 in Table 3). Slow reductions have been also found for aryl ketones, including acetophenone and its *ortho*-, *meta*- and *para*-substituted derivatives (entries 5–10 in Table 3). It is apparent that the introduction of electron-withdrawing groups (Cl, Br) in the *para* or *meta* position of the aromatic ring allows faster conversions (entries 7–9 *vs.* 5). In addition, a contrary effect is observed with an electron-donor group (*i.e.* OMe; entry 6 *vs.* 5). Assuming that these catalytic transformations follow the classical pathway in which the ketone coordinates to hydride-ruthenium intermediates,[27] the observed effects seem to

Table 2 Catalytic activity in transfer hydrogenation of cyclohexanone of complexes **2**–**4a**,**b** and **5**–**7a**,**b**[a]

Entry	Catalyst	Yield[b] (%)	TOF_{50}[c]/h^{-1}
Ruthenium(II) complexes			
1	**2a**	54 (98)[d]	70
2	**2b**	29 (97)[e]	30
3	**3a**	21 (88)[e]	17
4	**3b**	21 (75)[e]	14
5	**4a**	9 (84)[e]	
6	**4b**	7 (47)[e]	–
Ruthenium(IV) complexes			
7	**5a**	92 (>99)[f]	1020
8	**5b**	71 (98)[d]	150
9	**6a**	95 (>99)[f]	1600
10	**6b**	76 (98)[d]	230
11	**7a**	94 (>99)[f]	1010
12	**7b**	72 (>99)[e]	200

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of cyclohexanone (0.2 M in ^{i}PrOH). Ketone/catalyst/NaOH ratio: 250/1/24. [b] Yield of cyclohexanol after 2 h. GC determined. [c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at 50% conversion. [d] Yield after 9 h in parentheses. [e] Yield after 24 h in parentheses. [f] Yield after 4 h in parentheses.

Table 3 Catalytic transfer hydrogenation of ketones RR′C=O by complex **6a**[a]

Entry	R	R′	Yield[b] (%)	TOF_{50}[c]/h^{-1}
1	$-(CH_2)_6-$		95 (>99)[d]	1600
2	$-(CH_2)_5-$		86 (98)[e]	480
3	Me	Et	58 (96)[f]	90
4	Me	^{i}Pr	37 (76)[f]	30
5	Me	Ph	39 (91)[f]	30
6	Me	4-MeO-C_6H_4	31 (73)[f]	20
7	Me	4-Cl-C_6H_4	66 (96)[e]	140
8	Me	4-Br-C_6H_4	56 (98)[f]	90
9	Me	3-Br-C_6H_4	64 (99)[f]	130
10	Me	2-Br-C_6H_4	37 (42)[f]	–

[a] Conditions: reactions were carried out at 82 °C using 5 mmol of ketone (0.2 M in ^{i}PrOH). Ketone/catalyst/NaOH ratio: 250/1/24. [b] Yield of the corresponding alcohol after 2 h. GC determined. [c] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at 50% conversion. [d] Yield after 4 h in parentheses. [e] Yield after 9 h in parentheses. [f] Yield after 24 h in parentheses.

indicate that the hydride transfer from the metal to the coordinated ketone is the turnover-limiting step (rather than the ketone complexation) in the catalytic cycle.[29]

Experimental

General comments

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$,[30] $[\{Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$[31] and $(RO)_2P(=S)N_3$ (R = Et, Ph)[13] which were prepared by following the methods reported in the literature. Analytical and spectroscopic data for all the compounds reported in this paper have been provided as Electronic Supplementary Information (ESI †).

Preparations

$Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ (R = Et 1a, Ph 1b). The corresponding azide $(RO)_2P(=S)N_3$ (5.2 mmol) was added at −78 °C to a solution of bis(diphenylphosphino)methane (2 g, 5.2 mmol) in THF (80 cm^3). The reaction mixture was slowly warmed to room temperature and then evaporated to dryness to give a colorless oil. A microcrystalline white solid was obtained by slow diffusion of *n*-pentane into a saturated solution of the product in dichloromethane at room temperature. **1a**: Yield: 2.69 g, 94%. **1b**: Yield: 2.99 g, 89%.

$[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et 2a, Ph 2b). A solution of $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ (0.245 g, 0.4 mmol) and the corresponding iminophosphoranephosphine $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ **1a**,**b** (0.85 mmol) in dichloromethane (30 cm^3) was stirred at room temperature for 1 h. The solution was then concentrated (*ca.* 2 cm^3) and diethyl ether (50 cm^3) was added yielding an orange microcrystalline solid which was washed with diethyl ether (3 × 10 cm^3) and vacuum-dried. **2a**: Yield: 0.611 g, 89%. **2b**: Yield: 0.687 g, 90%.

$[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ (R = Et 3a, Ph 3b). *Method A.* A solution of the corresponding neutral complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ **2a**,**b** (0.5 mmol) in dichloromethane (50 cm^3) was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.172 g, 0.5 mmol) for 1 h. After the AgCl formed was filtered off (Kieselguhr), the solution was concentrated (*ca.* 2 cm^3) and diethyl ether (50 cm^3) was then added yielding an orange microcrystalline solid which was washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. **3a**: Yield: 0.423 g, 80%. **3b**: Yield: 0.554 g, 96%.

Method B. A suspension of $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ (0.122 g, 0.2 mmol), the corresponding iminophosphoranephosphine $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ **1a**,**b** (0.43 mmol) and $AgSbF_6$ (0.137 g, 0.4 mmol) in dichloromethane (30 cm^3) was stirred, at room temperature and in the absence of light, for 1.5 h. Work-up as described in *Method A* allows the isolation of **3a**,**b** in 83 (0.351 g) and 93% (0.429 g) yield, respectively.

$[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]_2$ (R = Et 4a, Ph 4b). *Method A.* A solution of the corresponding neutral complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ **2a**,**b** (0.5 mmol) in dichloromethane (50 cm^3) was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.378 g, 1.1 mmol) for 1 h. After the excess of $AgSbF_6$ used and the AgCl formed were filtered off (Kieselguhr), the solution was concentrated (*ca.* 2 cm^3) and diethyl ether (50 cm^3) was then added yielding an orange microcrystalline solid which was washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. **4a**: Yield: 0.585 g, 93%. **4b**: Yield: 0.650 g, 96%.

Method B. A solution of $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ **3a**,**b** (0.5 mmol) in dichloromethane (50 cm^3) was treated, at room temperature and in the absence of light, with $AgSbF_6$ (0.189 g, 0.55 mmol) for 1 h. Work-up as described in *Method A* allows the isolation of **4a**,**b** in 92 (0.579 g) and 90% (0.609 g) yield, respectively.

$[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ (R = Et 5a, Ph 5b). Complexes **5a**,**b**, isolated as orange microcrystalline solids, were prepared as described for **2a**,**b** starting from $[\{Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$ (0.246 g, 0.4 mmol) and the corresponding iminophosphorane-phosphine $Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2$ **1a**,**b** (0.85 mmol). **5a**: Yield: 0.674 g, 98%. **5b**: Yield: 0.749 g, 98%.

$[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ (R = Et 6a, Ph 6b). Complexes **6a**,**b**, isolated as orange microcrystalline solids, were prepared as described for **3a**,**b** starting either from $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ **5a**,**b** (0.5 mmol; *Method A*) or $[\{Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-Cl})Cl\}_2]$ (0.123 g, 0.2 mmol; *Method B*). **6a**: Yield (*Method A*): 0.509 g, 96%; Yield (*Method B*): 0.382 g, 90%. **6b**: Yield (*Method A*): 0.520 g, 90%; Yield (*Method B*): 0.430 g, 93%.

$[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]_2$ (R = Et 7a, Ph 7b). Complexes **7a**,**b**, isolated as yellow microcrystalline solids, were prepared as described for **4a**,**b** starting either from $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl_2(\kappa^1\text{-}P\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)]$ **5a**,**b** (0.5 mmol; *Method A*) or $[Ru(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})Cl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)][SbF_6]$ **6a**,**b** (0.5 mmol; *Method B*). **7a**: Yield (*Method A*): 0.510 g, 81%; Yield (*Method B*): 0.491 g, 78%. **7b**: Yield (*Method A*): 0.557 g, 82%; Yield (*Method B*): 0.542 g, 80%.

$[Ru(\eta^6\text{-}p\text{-cymene})(N{\equiv}CMe)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]_2$ 8. A solution of complex **4a** (0.629 g, 0.5 mmol) in acetonitrile (30 cm^3) was stirred at room temperature for 1 h and then evaporated to dryness. The resulting yellow oil was dissolved in 10 cm^3 of dichloromethane. Addition of diethyl ether (50 cm^3) afforded a microcrystalline solid which was washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. Yield: 0.539 g, 83%.

$[Ru(\eta^6\text{-}p\text{-cymene})(PR_3)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OEt)_2\}Ph_2)][SbF_6]_2$ (PR_3 = PMe_3 9, PMe_2Ph 10, $PMePh_2$ 11). A solution of complex **4a** (0.629 g, 0.5 mmol) and the appropriate phosphine (5 mmol) in dichloromethane (30 cm^3) was stirred at

room temperature for 5 (complex **9**), 6 (complex **10**) or 7 h (complex **11**) and then concentrated to *ca.* 5 cm^3. Addition of diethyl ether (40 cm^3) afforded a yellow microcrystalline solid which was washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. **9**: Yield: 0.640 g, 96%. **10**: Yield: 0.558 g, 80%. **11**: Yield: 0.634 g, 87%.

[Ru(η⁶-*p*-cymene)X(κ²-*P,S*-Ph_2PCH_2P{=NP(=S)(OEt)$_2$}Ph_2)][SbF_6] (X = Br 12, I 13, N_3 14). *Method A.* A solution of complex **4a** (0.629 g, 0.5 mmol) and the appropriate sodium salt NaX (5 mmol) in methanol (50 cm^3) was stirred at room temperature for 1 h and then evaporated to dryness. The residue was extracted with *ca.* 50 cm^3 of dichloromethane, the suspension filtered through Kieselguhr, and the resulting solution concentrated to *ca.* 2 cm^3. Addition of diethyl ether (40 cm^3) afforded an orange microcrystalline solid which was washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. **12**: Yield: 0.491 g, 89%. **13**: Yield: 0.552 g, 96%. **14**: Yield: 0.479 g, 90%.

Method B. A solution of complex **3a** (0.529 g, 0.5 mmol) and the appropriate sodium salt NaX (5 mmol) in methanol (50 cm^3) was stirred at room temperature overnight and then evaporated to dryness. Work-up as described in *Method A* allows the isolation of compounds **12**–**14** in 85 (0.468 g), 87 (0.501 g) and 80% (0.426 g) yield, respectively.

General procedure for catalytic transfer hydrogenation of ketones

Under an inert atmosphere the ketone (5 mmol), the ruthenium catalyst precursor (0.02 mmol, 0.4 mol%), and propan-2-ol (20 cm^3) were introduced into a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min. Then NaOH was added (5 cm^3 of a 0.096 M solution in propan-2-ol, 9.6 mol%) and the reaction monitored by gas chromatography. The corresponding alcohol and acetone were the only products detected in all cases.

X-Ray crystal structure of [Ru(η³:η³-$C_{10}H_{16}$)Cl(κ²-*P,S*-Ph_2-PCH_2P{=NP(=S)(OEt)$_2$}Ph_2)][BF_4]·$2CH_2Cl_2$·C_5H_{12} (the cation of 6a)

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of the complex in dichloromethane. Data collection, crystal, and refinement parameters are collected in Table 4. Diffraction data were recorded on a Nonius Kappa CCD single crystal diffractometer using Cu-Kα radiation (λ = 1.54184 Å). The crystal–detector distance was fixed at 29 mm and a total of 1130 frames were collected using the oscillation method, with 2° oscillation and 25 s exposure time per frame. Data collection strategy was calculated with the program Collect.[32] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[33] Unit cell dimensions were determined from 8421 reflections. All data completeness was 96.2%.

The structure was solved by Patterson methods using the program DIRDIF.[34] An empirical absorption correction was applied using XABS2.[35] Full-matrix least-squares refinement on F^2 was carried out with SHELXL-97.[36] All non-H atoms were anisotropically refined with the exception of the alternative partially occupied positions C42 and C42A atoms of the disordered *n*-pentane solvent molecule which were isotropically refined. The H atoms were geometrically placed and their coordinates were refined riding on their parent atoms. The maximum shift-to-e.s.d. ratio in the last full-matrix least-squares cycle was 0.000. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[37] Geometrical calculations were made with PARST.[38] The crystallographic plots were made with PLATON.[39] All calculations were performed at the Scientific Computer Centre of the University of Oviedo using VAX and DEC-ALPHA computers.

CCDC reference number 210707.

Table 4 Crystal data and structure refinement for **6a**

Empirical formula	$RuC_{46}H_{64}Cl_5F_4P_3O_2BNS$
Formula weight	1153.08
Temperature/K	120.0(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.1739(6)
b/Å	23.8656(9)
c/Å	21.1320(8)
α/°	90
β/°	125.00(9)
γ/°	90
Volume/Å³	5029(6)
Z	4
Calculated density/g cm^{-3}	1.523
Absorption coefficient/mm^{-1}	6.705
F(000)	2376
Reflections collected/unique	66067/9349 [*R*(int) = 0.059]
Goodness-of-fit on F^2	1.090
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0708$, $wR_2 = 0.2102$
R indices (all data)	$R_1 = 0.0863$, $wR_2 = 0.2525$
Largest diff. peak and hole/e Å^{-3}	2.040 and −1.315

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

See http://www.rsc.org/suppdata/dt/b3/b305520e/ for crystallographic data in CIF or other electronic format.

Computational details

All calculations were carried out with the Gaussian98 program package.[40] The molecular geometries were optimized, without any molecular symmetry constraint, using Schlegel's analytical gradient procedure[41] at the B3-LYP variant of density functional theory[42] with the standard split-valence 6-31G(d) basis set for C, N, O, and H,[43] and the pseudo-relativistic effective core potential (ECP) by Hay and Wadt for Ru, P, S, and Cl.[44] This basis set was referred to as DZV(d). The optimized structures were characterized as minima (representing equilibrium structures) by analytic frequency calculations. Single-point calculations on the DFT geometries were performed with the incorporation of correlation energy using Møller–Plesset perturbation theory with second-order corrections (MP2).[45]

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